

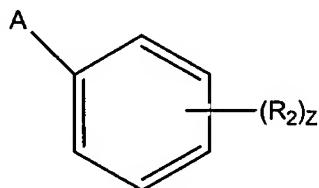


PATENT
514413-3915

AMENDMENTS TO THE CLAIMS

I. (Original) A method of reducing phytotoxicity to a crop (especially maize) at a locus caused by the application thereto of a herbicidal benzoylisoxazole and/or dione 5 derivative of formula (I):

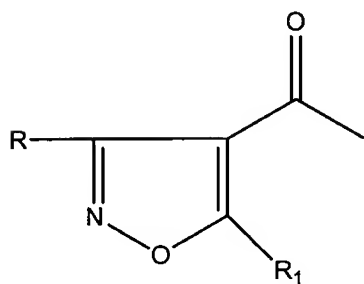
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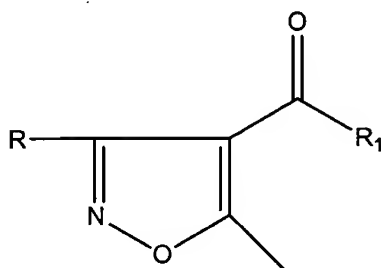
(I)

wherein:

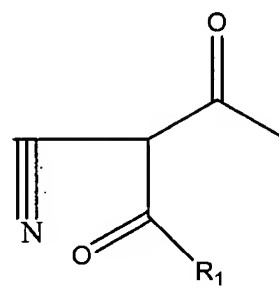
A is a group (A-1) to (A-7):



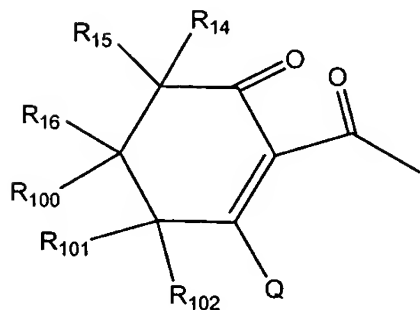
(A-1)



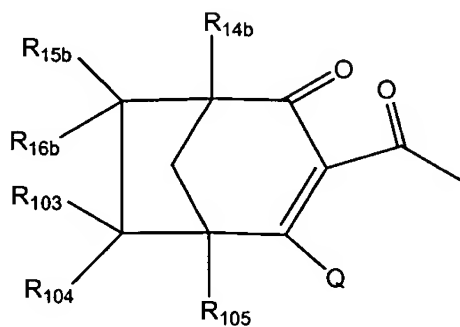
(A-2)



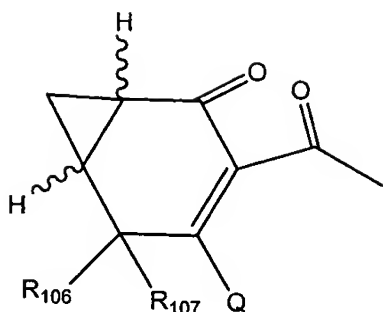
(A-3)



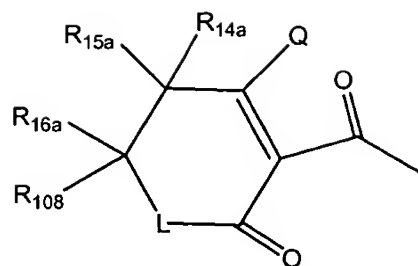
(A-4)



(A-5)

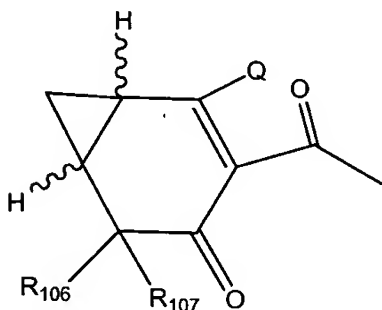


(A-6)

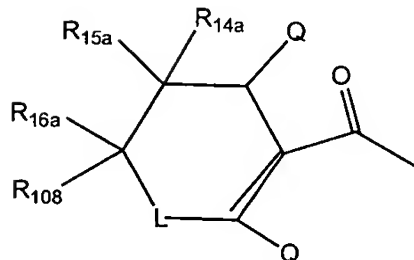


(A-7)

or a corresponding formula (A-6a) or (A-7a):



(A-6a)



(A-7a)

in which the position of the carbonyl group and the group Q are reversed and the double bond in the ring is attached to the carbon atom attached to the group Q;

R is a hydrogen atom or a halogen atom; a straight- or branched chain alkyl, alkenyl or alkynyl group containing from one to six carbon atoms which is optionally substituted by one or more halogen atoms; a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R^5 , one or more halogen atoms or a group $-CO_2R^3$; or a group selected from $-CO_2R^3$, COR^5 , cyano, nitro, $-CONR^3R^4$ and $-S(O)_kR^{13}$;

R^1 is a straight- or branched-chain alkyl, alkenyl or alkynyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms; or a cycloalkyl group containing from three to six carbon atoms optionally substituted by one or more groups R^5 or one or more halogen atoms;

R^2 is a halogen atom; a straight- or branched-chain alkyl, alkenyl or alkynyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms; a straight- or branched-chain alkyl group containing up to six carbon atoms which is substituted by one or more groups $-OR^5$; or a group selected from nitro, cyano, $-CO_2R^5$, $-S(O)_pR^6$, $-O(CH_2)_mOR^5$, $-COR^5$, $-NR^{11}$, R^{12} , $-N(R^8)SO_2R^7$, $-N(R^8)CO_2R^7$, $-OR^5$, $-OSO_2R^7$, $-SO_2NR^3R^4$, $-CONR^3R^4$, $-CSNR^3R^4$, $-(CR^9R^{10})_y-S(O)_qR^7$ and $-SF_5$;

or two groups R^2 , on adjacent carbon atoms of the phenyl ring may, together with the carbon atoms to which they are attached, form a 5 to 7 membered saturated or unsaturated heterocyclic ring containing up to three ring heteroatoms selected from nitrogen, oxygen and sulfur, which ring is optionally substituted by one or more groups selected from halogen, nitro, $-S(O)_pR^{13}$, $-C_{1-4}$ alkyl, C_{1-4} alkoxy, C_{1-4} haloalkyl, C_{1-4} haloalkoxy, $=O$ (or a 5- or 6-membered cyclic acetal thereof), and $=NO-R^3$, it being understood that a sulphur atom, where present in the ring, may be in the form of a group $-SO-$ or $-SO_2-$;

z is an integer from one to five: when z is greater than one the groups R^2 may be the same or different;

R^3 , R^4 and R^{109} are each independently a hydrogen atom, or a straight- or branched chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

R^5 and R^{110} are each independently a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms or a straight- or branched-chain alkenyl or alkynyl group containing from two to six (preferably from three to six) carbon atoms which is optionally substituted by one or more halogen atoms;

R^6 and R^7 , which may be the same or different, are each R^5 ; or phenyl optionally substituted by from one to five groups which may be the same or different selected from a halogen atom, a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms, nitro, cyano, $-\text{CO}_2R^5$, $-\text{S}(\text{O})_pR^{13}$, $-\text{NR}^{11}\text{NR}^{12}$, $-\text{OR}^5$ and $-\text{CONR}^3R^4$;

R^8 , R^9 and R^{10} are each a hydrogen atom or R^6 ;

R^{11} and R^{12} are each a hydrogen atom or R^5 ;

R^{13} and R^{111} are each a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

Q is hydroxy, C_{1-6} alkoxy, OR^{112} , SR^{112} or SR^{111} ;

L is oxygen or NR^{109} ;

R^{14} , R^{14a} , R^{14b} , R^{15} , R^{15a} , R^{15b} , R^{16} , R^{16a} , R^{16b} , R^{100} , R^{101} , R^{102} , R^{103} , R^{104} , R^{105} , R^{106} ,

R^{107} and R^{108} are each the same or different groups selected from hydrogen, R^{110} ,

$-(\text{CH}_2)_u\text{CO}_2R^{109}$, halogen, cyano, C_{1-6} alkoxy, $-(\text{CH}_2)_x$ -[phenyl optionally substituted by from one to five groups R^{113} which may be the same or different], and cycloalkyl containing from three to six carbon atoms optionally substituted by C_{1-6} alkyl or $-\text{S}(\text{O})_pR^{111}$;

R^{112} is phenyl optionally substituted by from one to five groups selected from halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy and nitro;

R^{113} is a group selected from halogen, R^{114} , nitro, cyano, $-CO_2R^{115}$, $-S(O)_pR^{111}$, $-OR^{111}$ and $-NR^{115}R^{116}$;

R^{114} is a straight- or branched- chain alkyl group containing one to three carbon atoms optionally substituted by one or more halogen atoms;

R^{115} and R^{116} which may be the same or different, are each a hydrogen atom or R^{110} ;

p , q and u are each independently zero, one or two;

k and m are each one, two or three;

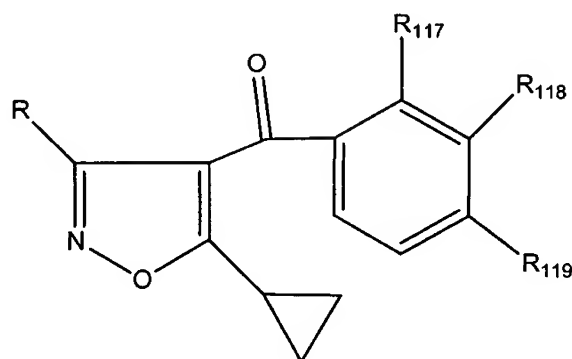
x is zero or one;

y is an integer from one to four; when y is greater than one, the groups R^9 and

R^{10} may be the same or different;

or an agriculturally acceptable salt or metal complex thereof; which method comprises applying to the locus of the crop, preferably before the herbicidal compound, an antidotally effective amount of an antidote compound, and optional partner herbicide.

2. (Original) A method according to claim 1 in which the isoxazole or dione herbicide has the general formula (Ia):



(Ia)

are those wherein:

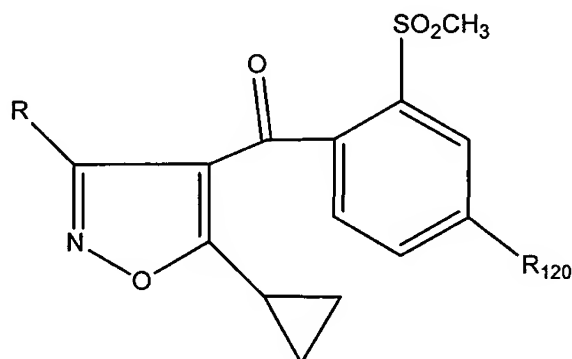
R is hydrogen or $-CO_2Et$;

R^{117} is selected from $-S(O)_pMe$, Me, Et, a chlorine, bromine or fluorine atom, methoxy, ethoxy and $-CH_2S(O)_qMe$;

R^{118} is selected from a hydrogen atom, a chlorine, bromine or fluorine atom, methoxy, ethoxy and $-S(O)_pMe$;

R^{119} is selected from a hydrogen atom, a chlorine, bromine or fluorine atom, methoxy, CF_3 ; and p and q each independently have the values zero, one or two.

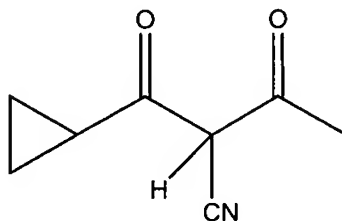
3. (Original) A method according to claim 1 or 2 in which the isoxazole or dione herbicide has the general formula (Ib):



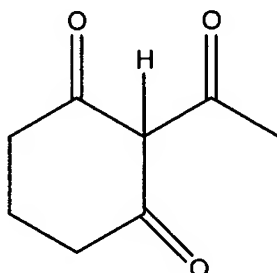
(Ib)

wherein R^{120} is chlorine, bromine or trifluoromethyl; and R is hydrogen or $-CO_2Et$.

4. (Original) A method according to any one of the preceding claims in which a substituted phenyl ring as defined in formulae (I); (Ia); or (Ib) as depicted in claim 1, 2 or 3 is attached to a grouping;



5. (Original) A method according to claim 4 in which the phenyl ring is substituted by two groups independently selected from halogen, alkyl, S(O)_palkyl (p = 0, 1 or 2) or haloalkyl.
6. (Original) A method according to claim 1, 2 or 3 in which a substituted phenyl ring as defined above in formula (I); (Ia); or (Ib) is attached to a grouping;



7. (Original) A method according to claim 1 wherein the compound of formula (I) is:
- 5-cyclopropyl-4-[2-chloro-3-ethoxy-4-(ethylsulphonyl)benzoyl]isoxazole;
- 4-(4-chloro-2-methylsulphonylbenzoyl)-5-cyclopropylisoxazole;
- 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole;
- 4-(4-bromo-2-methylsulphonylbenzoyl)-5-cyclopropylisoxazole;
- 5-cyclopropyl-4-[4-fluoro-3-methoxy-2-(methylsulphonyl)benzoyl]isoxazole;
- 4-(4-bromo-2-methylsulphonylmethylbenzoyl)-5-cyclopropylisoxazole;
- ethyl 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl) isoxazole-3-carboxylate;
- 2-[2-chloro-(4-methylsulphonyl)benzoyl]-1,3-cyclohexanedione;
- 2-[2-nitro-(4-methylsulphonyl)benzoyl]-1,3-cyclohexanedione;
- 2-(2,3-dihydro-5,8-dimethyl-1,1-dioxospiro[4H-1-benzothiine-4,2' [1,3]dioxolan]-6-ylcarbonyl)cyclohexane-1,3-dione;
- 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)-3-methylthio-isoxazole; and
- 2-cyano-3-cyclopropyl-1-(2-methylsulphonyl-4-trifluoromethylphenyl) propan-1,3-dione.

8. (Original) A method according to claim 7 in which the compound is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole or 2-[2-nitro-(4-methylsulphonylbenzoyl)-1,3-cyclohexanedione.
9. (Original) A method according to claim 1 in which the antidote is selected from: flurazole; fenclorazole-ethyl; fenclorazole; benoxacor; dichlormid; fenclorim; furilazole; mefenpyr-diethyl; CMPI; 4-hydroxy-1-methyl-3-(1-1*H*-tetrazol-5-ylmethanoyl)-1*H*-quinolin-2-one; daimuron; (S)-MBU; dimepiperate; 5,5-diphenylisoxazoline-3-carboxylic acid; and ethyl 5,5-diphenylisoxazoline-3-carboxylate.
10. (Original) A method according to claim 1 in which the antidote is selected from fenclorazole; CMPI; 4-hydroxy-1-methyl-3-(1-1*H*-tetrazol-5-ylmethanoyl)-1*H*-quinolin-2-one; (S)-MBU and dimepiperate.
11. (Original) A method according to any one of the preceding claims in which the crop plant to be protected is maize.
12. (Original) A method according to claim 1 in which the application rate of the benzoylisoxazole and/or dione of formula (I) is from 0.004 kg to 5 kg per hectare.
13. (Original) A method according to claim 1 in which the application rate of the benzoylisoxazole and/or dione of formula (I) is from 0.01 kg to 2 kg per hectare.
14. (Original) A method according to any one of the preceding claims in which (a) the herbicidal benzoylisoxazole and/or dione derivative and (b) antidote are applied separately such that the antidote contacts the seed or plant being treated before the herbicidal compound.
15. (Original) A herbicidal composition comprising:
 - (a) a herbicidally effective amount of a benzoylisoxazole and/or dione derivative of formula (I) or an agriculturally acceptable salt or metal complex thereof,

optionally in combination with a partner herbicide; and

- (b) an antidotally effective amount of an antidote compound;

in association with a herbicidally acceptable diluent or carrier and/or surface active agent.

16. (Original) A composition according to claim 15 which comprises the component (a) as a delayed release formulation.

17. (Original) A composition according to claim 15 or 16 in which the weight ratio of the compound of formula (I): antidote is from 1:25 to 60:1.

18. (Original) A product comprising:

- (a) a herbicidally effective amount of a benzoylisoxazole and/or dione derivative of formula (I), or an agriculturally acceptable salt or metal complex thereof; and

- (b) an antidotally effective amount of an antidote;

wherein said antidote is antidotally effective to said benzoylisoxazole and/or dione derivative; as a combined preparation for separate, simultaneous or sequential use in the control of weeds at a locus.

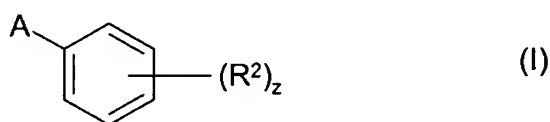
19. (Original) A product according to claim 18 as a combined preparation for use in which the antidote contacts the seed or plant being treated before the herbicidal compound.

20. (Original) A method according to claim 1 substantially as hereinbefore described.

21. (Original) A composition according to claim 15 substantially as hereinbefore described.

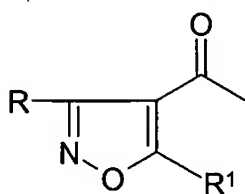
22. (Original) A product according to claim 18 substantially as hereinbefore described.

23. (New) A method of reducing phytotoxicity to a crop at a locus caused by the application thereto of a herbicidal benzoylisoxazole and/or dione derivative of formula (I):

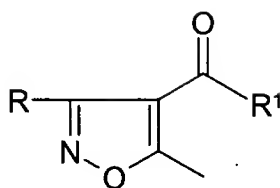


wherein

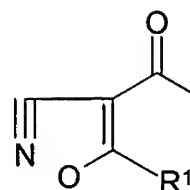
A is a group (A-1), (A-2) or (A-3):



(A-1)



(A-2)



(A-3)

R is a hydrogen atom or a halogen atom; a straight- or branched chain alkyl, alkenyl or alkynyl group containing from one to six carbon atoms which is optionally substituted by one or more halogen atoms; a cycloalkyl group containing from 3 to 6 carbon atoms optionally substituted by one or more groups R^5 , one or more halogen atoms; or a group selected from $-\text{CO}_2R^3$, $-\text{COR}^5$, cyano, nitro, $-\text{CONR}^3R^4$ and $-\text{S(O)}_kR^{13}$;

R^1 is straight- or branched-chain alkyl, alkenyl or alkynyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms; or a cycloalkyl group containing from three to six carbon atoms optionally substituted by one or more groups R^5 or one or more halogen atoms;

R^2 is a halogen atom; a straight- or branched-chain alkyl, alkenyl or alkynyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms; a straight- or branched-chain alkyl group containing up to six carbon atoms which is substituted by one or more groups $-\text{OR}^5$ or a group selected from nitro, cyano, $-\text{CO}_2R^5$, $-\text{S(O)}_pR^6$, $-\text{O}(\text{CH}_2)_m\text{OR}^5$, $-\text{COR}^5$, $-\text{NR}^{11}R^{12}$, $-\text{N(R}^8)\text{SO}_2R^7$, $-\text{N(R}^8)\text{CO}_2R^7$, $-\text{OR}^5$, $-\text{OSO}_2R^7$, $-\text{SO}_2R^7$, $-\text{SO}_2\text{NR}^3R^4$, $-\text{CONR}^3R^4$, $-\text{CSNR}^3R^4$, $-(\text{CR}^9R^{10})_y-\text{S(O)}_qR^7$ and $-\text{SF}_5$;

or two groups R^2 , on adjacent carbon atoms of the phenyl ring may, together with the carbon atoms to which they are attached, form a 5 to 7 membered saturated or unsaturated heterocyclic ring containing up to three ring heteroatoms selected from nitrogen, oxygen and sulfur, which ring is optionally substituted by one or more groups selected from halogen, nitro, $-S(O)_qR^{13}$, C_{1-4} alkyl, C_{1-4} alkoxy, C_{1-4} haloalkyl, C_{1-4} haloalkoxy, $=O$ (or a 5- or 6- membered cyclic acetal thereof), and $=NO-R^3$, it being understood that a sulphur atom, where at present in the ring, may be in the form of a group $-SO-$ or $-SO_2-$;

z is an integer from one to five: when z is greater than one the groups R^2 may be the same or different;

R^3 and R^4 are each independently a hydrogen atom, or a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

R^5 is a straight- or branched-chain alkyl group containing up to six atoms which is optionally substituted by one or more halogen atoms or a straight- or branched-chain alkenyl or alkynyl group containing from two to six carbon atoms which is optionally substituted by one or more halogen atoms;

R^6 and R^7 , which may be the same or different, are each R^5 ; or phenyl optionally substituted by from one to five groups which may be the same or different selected from a halogen atom, a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms, nitro, cyano, $-CO_2R^5$, $S(O)_pR^{13}$, $-NR^{11}NR^{12}$, $-OR^5$ and $-CONR^3R^4$;

R^8 , R^9 and R^{10} are each a hydrogen atom or R^6 ;

R^{11} and R^{12} are each a hydrogen atom or R^5 ;

R^{13} is a straight- or branched-chain alkyl group containing up to six carbon atoms which is optionally substituted by one or more halogen atoms;

p and q are each independently zero, one or two;

k and m are each one, two or three;

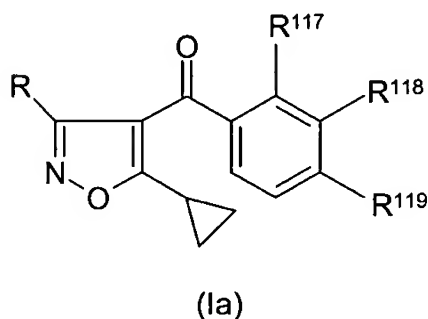
y is an integer from one to four; when y is greater than one; the groups R^9 and R^{10} may be the same or different;

or an agriculturally acceptable salt or metal complex thereof;

which method comprises applying to the locus of the crop before the herbicidal compound an antidotally effective amount of an antidote compound, and optionally partner herbicide,

wherein the antidotally compound is a compound selected from the group consisting of ethyl 5,5-diphenylisoxazoline-3-carboxylate and 5,5-diphenylisoxazoline-3-carboxylic acid.

24. (New) A method according to claim 23 wherein the compound of formula (I) is a compound of the formula (Ia):



wherein:

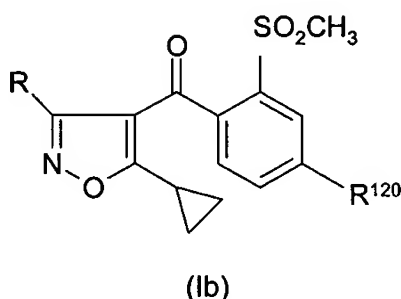
R is hydrogen or $-\text{CO}_2\text{Et}$;

R^{117} is selected from $-\text{S}(\text{O})_p\text{Me}$, Me, Et, a chlorine, bromine or fluorine atom, methoxy, ethoxy and $-\text{CH}_2\text{S}(\text{O})_q\text{Me}$;

R^{118} is selected from a hydrogen atom, a chlorine, a bromine or fluorine atom, methoxy, ethoxy and $-S(O)_pMe$;

R^{119} is selected from a hydrogen atom, a chlorine, a bromine or fluorine atom, methoxy and CF_3 ; and p and q each independently have the values zero, one or two.

25. (New) A method according to claim 24 in which the compound of the formula (I) is a



compound of formula (Ib):

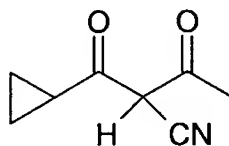
wherein R^{120} is chlorine, bromine or trifluoromethyl; and R is hydrogen or $-CO_2Et$.

26. (New) A method according to claim 25 in which the compound of the formula (I) is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole.

27. (New) A method according to claim 26 in which the antidote compound is ethyl 5,5-diphenylisoxazoline-3-carboxylate.

28. (New) A method according to claim 26 in which the antidote compound is 5,5-diphenylisoxazoline-3-carboxylic acid.

29. (New) A method according to claim 23 wherein A in formula (I) is a group of the formula



30. (New) A method according to claim 29 in which the antidote compound is ethyl 5,5-diphenylisoxazoline-3-carboxylate.

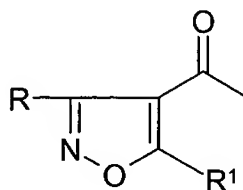
31. (New) A method according to claim 29 in which the antidote compound is 5,5-diphenylisoxazoline-3-carboxylic acid.

32. (New) A method according to claim 30 wherein $(R^2)_z$ in formula (I) is 2-methylsulfonyl-4-trifluoromethyl.

33. (New) A method according to claim 31 wherein $(R^2)_z$ in formula (I) is 2-methylsulfonyl-4-trifluoromethyl.

34. (New) A method as claimed in claim 23, wherein in the compound of formula (I):

A is a group (A-1):



(A-1)

in which R is $-S(O)_kR^{13}$.

35. (New) A method as claimed in claim 34, wherein

R is $SO-R^{13}$ or SO_2R^{13} ,

R^1 is cyclopropyl, and

R^{13} is an alkyl group containing up to six carbon atoms.

36. (New) A herbicidal composition comprising

(a) a herbicidally effective amount of a compound of formula (I) as defined in claim 23 or an agriculturally acceptable salt or metal complex thereof, optionally in combination with a partner herbicide; and

(b) an antidotally effective amount of an antidote compound selected from ethyl 5,5-diphenylisoxazoline-3-carboxylate and 5,5-diphenylisoxazoline-3-carboxylic acid.

37. (New) A herbicidal composition as claimed in claim 36 wherein the herbicidal compound of formula (I) is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethylbenzoyl)isoxazole.

38. (New) A herbicidal composition as claimed in claim 37 wherein the antidote compound is ethyl 5,5-diphenylisoxazoline-3-carboxylate.

39. (New) A herbicidal composition as claimed in claim 37 wherein the antidote compound is 5,5-diphenylisoxazoline-3-carboxylic acid.

40. (New) A herbicidal composition as claimed in claim 39 wherein the weight ratio of the compound of formula (I) : antidote is from 1:25 to 60:1.